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XIX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF NITRIC ACID ON SYMMETRICAL TRICHLORBENZOL.

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Presented March 9, 1887.

WE were led to take up the study of this subject by our work upon the constitution of benzoltrisulphonic acid, described in the preceding paper, since the trichlorbenzol derived from that substance by replacing its sulpho groups with chlorine, although melting at 63° like the symmetrical compound (melting point 63°.5 according to Beilstein and Kurbatow*), gave on treatment with nitric acid a body melting at 130°, whereas Beilstein and Kurbatow obtained in this way trichlormononitrobenzol,† melting point 68°. To find the cause of this discrepancy we have prepared the symmetrical trichlorbenzol, and treated it with nitric acid in the cold, when we found that the product was the substance melting at 130° (or more accurately at 129°.5) mentioned above, which proved on analysis to be trichlordinitrobenzol. This result was the more strange, because our nitric acid had a specific gravity of only 1.505, whereas that used by Beilstein and Kurbatow showed 1.52, and in order to get their trichlormononitrobenzol we found it necessary to dilute our acid to 1.46. Since these experiments seemed to show that our nitric acid was more efficient in its action than that used by Beilstein and Kurbatow, we determined to study the subject more carefully, and next attempted the preparation of the trichlortrinitrobenzol, which we obtained without difficulty by boiling the trichlordinitrobenzol for about two hours with a mixture of our nitric acid and fuming sulphuric acid. Both this substance and the dinitro compound are new, the difficulty of the preparation of symmetrical trichlorbenzol having prevented a thorough study of this substance. On the other hand, the corresponding tribrombenzol can be made with great ease, and, as its action with fuming nitric acid has been studied frequently, we decided to extend our experiments to it to see whether in this case also our nitric acid proved more reactive than that of the chemists who have worked in this field heretofore. The complete description of our results with tribrombenzol will be postponed till a later paper, and we shall give here only that portion of them which shows that the action of our nitric acid on the tribrombenzol is similar to its action on the trichlorbenzol, prefacing it with a brief historical sketch of the work of our predecessors.

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* Ann. Chem., cxcii. 233.

† Ber. d. ch. G., 1877, p. 271.

Koerner * was the first (in 1874) who studied this subject, obtaining on dissolving the symmetrical tribrombenzol with the aid of heat in nitric acid of specific gravity 1.54 the dinitro compound, with a mixture of fuming sulphuric acid and nitric acid the trinitro compound, while all his attempts to obtain the mononitro derivative by direct nitriring failed, owing to the insolubility of the tribrombenzol in weaker acid. In the next year † one of us ‡ working in the laboratory of Berlin found that the fuming nitric acid supplied in that laboratory converted tribrombenzol into the mononitro compound only when boiled with it, and that it was necessary to use a boiling mixture of nitric and (common) sulphuric acids to obtain the dinitro derivative. These observations were confirmed a few years later by Wurster and Beran,§ who obtained only the mononitro compound from the action of a nitric acid of 1.534 specific gravity alone, and the dinitro compound when its action was reinforced by mixture with crystallized fuming sulphuric acid. Even when this mixture was heated with tribrombenzol in sealed tubes to 220° for 48–60 hours, only a very minute quantity of a trinitro compound was formed; which led them to the conclusion that the trinitro derivative mentioned but not described by Koerner could not be obtained.

In taking up again the study of the nitro compounds of symmetrical tribrombenzol we used the nitric acid of specific gravity 1.505–1.51,

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* Gazz. Chim., iv. 422, 425.

† Von Richter (Ber. d. ch. G., 1875, p. 1426) succeeded in obtaining the mononitro compound by boiling glacial acetic acid and tribrombenzol with nitric acid of specific gravity 1.52, but found, in agreement with Koerner, that an acid of 1.54 boiled with tribrombenzol converted it into the dinitro compound.

‡ Jackson, Ber. d. ch. G., 1875, p. 1172.

§ Ber. d. ch. G., 1879, p. 1821.

which had acted on trichlorbenzol in the way already described, and found that this acid converted the tribrombenzol, even when the mixture was carefully cooled, direct into tribromdinitrobenzol, no mononitro compound being formed; and further, that by the action of a mixture of this nitric acid with fuming sulphuric acid on tribromdinitrobenzol the tribromtrinitrobenzol, melting point 285°, was formed without difficulty in open vessels. We therefore confirm completely the results of Koerner, so far as they apply to the di and trinitro compounds, in opposition to those obtained by one of us, and by Wurster and Beran; and, to make the comparison more striking, we have used for these experiments tribrombenzol made from some tribromaniline prepared in Berlin by one of us during his previous experiments. To sum up the whole case in a few words, it appears that our nitric acid of specific gravity 1.505–1.51 is much more efficient in its action than the commercial fuming nitric acid used in the laboratories of St. Petersburg[*] (1.52), Berlin,[†] and Munich[‡] (1.534); and we are inclined to ascribe the high specific gravities of these commercial acids in part to the presence of lower oxides of nitrogen, while the specific gravity of our acid was due probably exclusively to HNO_3, since it was prepared in our laboratory directly from nitre and sulphuric acid, not pushing the reaction beyond the formation of acid potassic sulphate. This explanation is based upon the observation of Kolb,[§] that the specific gravity of nitric acid is raised by the solution of nitric dioxide in it; and although we cannot submit it to direct experimental proof, since commercial fuming nitric acid is not to be had in this country, yet the following examination of a nitric acid similar to that used in foreign laboratories makes it exceedingly probable that this explanation is correct. This acid was prepared by distilling common nitric acid twice with an excess of sulphuric acid; it had a decided yellow color, and a specific gravity of 1.535 at 15° (the temperature at which all our determinations were made), but converted tribrombenzol into tribrommononitrobenzol only, when acting in the cold, although it gave the dinitro compound when boiled with it. It was therefore less efficient than our acid of specific gravity 1.51, but more so than the foreign acids mentioned above. The analyses of this acid and of our acid of 1.51 specific gravity yielded the following results, which are given in tabular form to facilitate comparison.

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[*] Beilstein and Kurbatow.

[†] Jackson.

[‡] Wurster and Beran.

[§] Ann. Chim. Phys., ser. 4, x. 137.

	Per Cent NO_2.	Per Cent HNO_3.	H_2O by Difference.
Acid of 1.535 sp. gr.	5.0	93.38	1.62
Acid of 1.51 sp. gr.	0.5	96.92 *	2.58

The nitric dioxide was determined in the usual way by treatment of the diluted acid with a standard solution of potassic permanganate. The results are not absolutely accurate, as observed by Feldhaus,† because of the loss of nitric dioxide in transferring the acid from the weighing or measuring tube to the beaker, but are nearly enough so for our purpose. The nitric acid was determined by neutralization with ammonic hydrate, and weighing the ammonic nitrate dried at 120°. It contained no ammonic nitrite. The estimated amount of nitric acid corresponding to the nitric dioxide found has been subtracted, so that the number given represents the percentage of free HNO_3 in the acid. These results show that the acid with the higher specific gravity contains the smaller amount of HNO_3, and therefore that the determination of the specific gravity is not a trustworthy way of finding the strength of nitric acid, unless the sample examined is free from lower oxides of nitrogen.

After the foregoing account of our work was already written we received a paper by Nietzki and Hagenbach,‡ in which a similar experience is described; for they found that with commercial fuming nitric acid a mononitro compound alone could be obtained from diacetylmetaphenylenediamine, whereas they obtained the dinitro compound by using "pure monohydrate," which, they say, can be prepared most easily by distilling fuming nitric acid with twice the quantity of sulphuric acid, and which had a specific gravity of 1.533 at 15°. It is to be observed, however, that our experiment with an acid prepared in a similar way shows that even this acid is not so pure as that made direct from nitre and sulphuric acid.

Preparation of Symmetrical Trichlorbenzol.

We have tried all of the three different processes known for making trichloraniline, viz.: 1st. By the direct action of chlorine on aniline dissolved in glacial acetic acid, — a method which gives the trichloraniline more quickly than any of the others, but which we discarded on account of the very small yield obtained. 2d. According to Beilstein and Kurbatow,* by the formation of chloracetanilid from chlorine and acetanilid, and converting this, after the removal of the acetyl, into trichloraniline by treatment with chlorine in a glacial acetic acid solution. We may be allowed to remark, in regard to this method, that we were unable to make acetanilid in glacial acetic acid solution take up more than one atom of chlorine, an excess of chlorine passing through the solution unaltered after monochloracetanilid had been formed, whereas Beilstein and Kurbatow obtained the dichloracetanilid in this way; we have not thought the point of sufficient importance, however, to devote to it the time necessary to determine the cause of this difference. This method gives good results, but does not lead to them so quickly and easily as the *third*, which consists in making dichloracetanilid according to Witt,† that is, acting on acetanilid in a warm acetic acid solution with a solution of bleaching-powder. The dichloracetanilid was then converted into the trichloraniline, as in the second method.

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* This number is higher than that given by Kolb as corresponding to this specific gravity (1.51), which is 94 per cent. The difference may be due to the presence of amines in the ammonia used by us; but we have not studied this point more carefully, as we are not interested in the absolute determination of the amount of HNO_3 in this acid, but only in the relative amounts of HNO_3 in these two nitric acids, which are given accurately by our numbers, since they were obtained under exactly parallel conditions.

† Zeitschr. Anal. Chem , i. 426.

‡ Ber. d. ch. G., 1887, p. 333.

The method, therefore, which we finally adopted, and should recommend as the best, is the following: 5 parts of acetanilid are dissolved in 20 parts of glacial acetic acid and 100 of water, and heated to boiling; then, after removing the lamp, a 10 per cent solution of bleaching-powder is added, until a viscous precipitate is formed, the temperature being kept above 70°. The precipitate is then treated with ammonic hydrate, and crystallized from alcohol. The yield of dichloracetanilid is nearly quantitative. The dichloracetanilid is next converted into dichloraniline by heating it on the water-bath with strong sulphuric acid, the dichloraniline dissolved in glacial acetic acid, and chlorine passed through the solution until two parts of the dichloraniline have gained one part of chlorine; the product is then rendered alkaline with a large excess of sodic hydrate, and distilled with steam; the solid which distils over, after crystallization from dilute alcohol, is pure trichloraniline, but the yield is far from satisfactory, a large quantity of tarry impurity being formed during the treatment of the free base with chlorine. The trichloraniline is converted into trichlorbenzol by the method of Bässmann;* that is, it is dissolved in alcohol of 95 per cent by heat, and the calculated amount of a hot concentrated aqueous solution of potassic nitrite added, and then dilute sulphuric acid, little by little, until the reaction is strongly acid; the mixture is then warmed gently on the water-bath until the reaction comes to an end, and the trichlorbenzol purified by crystallization from alcohol. The yield is good, 8 grm. of the trichloraniline giving 5 grm. of trichlorbenzol; that is, 67 per cent of the theoretical amount.

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* Ann. Chem., clxxxii. 95.

† Ber. d. ch. G., 1875, p. 1226. Bender, Ber. d. ch. G., 1886, p. 2272, has obtained $C_6H_5NClCOCH_3$ by the action of bleaching powder on a *cold* acetic acid solution of acetanilid.

Trichlordinitrobenzol, $C_6HCl_3(NO_2)_2$.

The symmetrical trichlorbenzol was dissolved in nitric acid† of specific gravity 1.505 at the ordinary temperature; the same result was also obtained if the beaker in which the reaction took place was kept cool by immersion in cold water. When the trichlorbenzol was completely dissolved, the product was precipitated by pouring it into cold water or snow, and purified by crystallization from hot alcohol until it showed the constant melting point 129°.5, when it was dried at 100° and analyzed.

0.2694 grm. of the substance gave 24.4 c.c. of nitrogen at 24° temperature and 766.5 mm. pressure.

0.2102 grm. of substance gave, according to the method of Carius, 0.3322 grm. of argentic chloride.

	Calculated for $C_6HCl_3(NO_2)_2$.	Found.
Nitrogen	10.31	10.24
Chlorine	39.22	39.07

Properties. — It forms thick, long white prisms, when crystallized from alcohol, which melt at 129°.5, and are soluble in cold alcohol, much more freely in hot, very easily soluble in benzol, chloroform, carbonic disulphide, or acetone, soluble in ether, or in glacial acetic acid, still more soluble in hot glacial acetic acid.

In order to obtain trichlormononitrobenzol, a nitric acid diluted until it shows the specific gravity 1.46 must be boiled with trichlorbenzol until complete solution takes place. After precipitation with water and recrystallization from alcohol, the product of such a preparation showed the melting point 68°, that given by Beilstein and Kurbatow. Ordinary strong nitric acid of specific gravity 1.4 has no action on trichlorbenzol, whether hot or cold.

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* Ann. Chem., cxci. 206.

† The nitric acid was prepared by distilling nitre with sulphuric acid in the proportions of one molecule of each. See page 374, for a discussion of this point.

The constitution of the trichlordinitrobenzol follows from the fact that it is made from symmetrical trichlorbenzol, and is

$$H : Cl : NO_2 : Cl : NO_2 : Cl = 1 : 2 : 3 : 4 : 5 : 6.$$

Trichlortrinitrobenzol, $C_6Cl_3(NO_2)_3$.

This substance was made by boiling in a flask, for half an hour or somewhat more, trichlordinitrobenzol with a mixture of fuming sulphuric acid and nitric acid of specific gravity 1.505, prepared direct from nitre and sulphuric acid.* The substance goes completely into solution while hot, but a considerable quantity separates out as it cools. The whole is then precipitated with snow, and treated with hot alcohol, when an insoluble residue containing sulphur is left behind; this is probably a sulphone, but was formed in such small quantities that we did not try to study it. The hot alcoholic solution on cooling deposits the trichlortrinitrobenzol, which is purified by crystallization from boiling alcohol until it shows the constant melting point 187°. The substance was dried at 100° and analyzed, with the following results.

0.1656 grm. of substance gave 18.8 c.c. of nitrogen at a temperature of 18° and 750 mm. pressure.

0.1486 grm. of substance gave, acording to the method of Carius, 0.2034 grm. of argentic chloride.

	Calculated for $C_6Cl_3(NO_2)_3$.	Found.
Nitrogen	13.27	12.94
Chlorine	33.64	33.83

Properties. — The trichlortrinitrobenzol is obtained by crystallization from alcohol in rather thick good-sized needles of a white color, with a slight yellowish tinge, melting point 187°, very nearly insoluble in water, but not completely so, less soluble in alcohol than trichlordinitrobenzol, easily soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide. Alcohol is the best solvent for it.

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* See page 374.

The constitution of the trichlortrinitrobenzol, since it is made from the symmetrical trichlorbenzol, is also symmetrical, —

$$Cl : NO_2 : Cl : NO_2 : Cl : NO_2 = 1 : 2 : 3 : 4 : 5 : 6.$$

The description of the tribromtrinitrobenzol, as well as of some of the derivatives of this very reactive substance, will be postponed until another paper.